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(54) Title: A METHOD OF INCREASING THE ADHESION BETWEEN RADIATION-CURED, INNER PRIMARY COATINGS AND OPTICAL GLASS FIBERS

(57) Abstract

The invention relates to a method of increasing the adhesion of a radiation-cured, inner primary, optical glass fiber coating on an optical glass fiber, said method comprising the steps of: 1) exposing at least a section of said optical glass fiber to electron beam radiation at a level sufficient to induce bonding with a radiation-curable, optical glass fiber coating composition; 2) applying said radiation-curable, optical glass fiber coating composition onto said electron beam exposed optical glass fiber, said coating composition containing at least one monomer or oligomer having a radiation-curable functional group which can form free radicals in the presence of actinic radiation; and 3) exposing said coated optical glass fiber to actinic radiation to thereby cure said inner primary coating.

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A METHOD OF INCREASING THE ADHESION BETWEEN RADIATION-CURED, INNER PRIMARY COATINGS AND OPTICAL GLASS FIBERS

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to a method of increasing the adhesion of radiation-cured, inner primary coatings on glass optical fibers. This invention further relates to a method of providing sections of a coated optical glass fiber with different levels of adhesion between the inner primary coating and each portion of the glass optical fiber. This invention also relates to optical glass fibers having enhanced adhesion between the inner primary coating and the optical glass fiber, and to an optical glass fiber having sections thereof with different levels of adhesion between the inner primary coating and each section of the glass optical fiber. The invention further relates to a glass optical fiber drawing tower having the flexibility to continuously adjust the adhesion of the inner primary coating to the optical glass fiber.

2. Description of Related Art

Optical glass fibers are frequently coated with two or more superposed radiation-curable coatings, which together form a primary coating. The coating which contacts the optical glass fiber is called the inner primary coating and the overlaying coating is called the outer primary coating. In other references, the inner primary coating may be called the primary coating and outer primary coating may be called the secondary coating.

The inner primary coating is usually a soft coating providing resistance to microbending. Microbending can lead to attenuation of the signal transmission capability of the coated optical glass fiber and is therefore undesirable. The outer primary coating, which may be the exposed outermost coated surface, is typically a harder coating providing desired resistance to handling forces, such as those encountered when the fiber is cabled.

Coating compositions for making inner primary coatings generally comprise a polyethylenically-unsaturated monomer or oligomer dissolved or dispersed in a liquid ethylenically- unsaturated medium and a photoinitiator. The inner primary coating composition is typically applied to the optical glass fiber in liquid form and then exposed to actinic radiation to cure and harden the inner primary coating composition.

In addition to causing the weakening of the optical glass fibers, moisture can also cause the inner primary coating layer to delaminate from the optical glass fiber. The delamination of the inner primary coating from the optical glass fiber usually results in a weakened optical glass fiber, because the delaminated inner primary coating can slide against the optical glass fiber causing microscopic scratches in the surface of the optical glass fiber. The microscopic scratches can be crack initiation points where cracks in the optical glass fiber can form thereby weakening the optical glass fiber. Furthermore, if the delamination of the inner primary coating is periodic, high transmission loss could be induced.

To reduce delamination of the inner primary coating caused by moisture, adhesion promoting additives have been incorporated in inner primary coating compositions. Inner primary coatings made from coating compositions without having adhesion promoters may generally be easily removed from glass optical

fibers after exposure to high humidity.

Compounds containing the following structures have been successfully utilized as adhesion promoters in inner primary coating compositions:

$$H_2C = C(CH_3)-C(=O)-O-(CH_2)_3-Si(OCH_3)_3$$

commercially available from Kay Fries, Inc. (MEMO™)

$$HS-(CH_2)_3-Si(OCH_3)_3$$

commercially available from Union Carbide, Inc. (A-189)

It is believed that the trimethoxysilyl group, $-Si(OCH_3)_3$ reacts with the surface of the optical glass fiber by the following reaction with silanol groups on the glass:

$$\text{glass-Si-OH} + H_3CO - Si(OCH_3)_2 - R \rightarrow \text{glass} - Si - O - Si(OCH_3)_2 - R + CH_3OH$$

The methacrylate group or the mercapto group present in "R" of the adhesion promoter molecule is believed to react with the inner primary coating during free radical polymerization, upon exposure to actinic radiation, through formation of a free radical entity as follows:

$$CH_2{=}\underset{\displaystyle CH_3}{\underset{|}{C}}{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}O{-}(CH_2)_3\ Si(OCH_3)_3 \quad + \quad \underset{\text{(propagating radical chain)}}{R^{\bullet}} \rightarrow$$

$$R{-}CH_2{-}\underset{\displaystyle CH_3}{\underset{|}{C^{\bullet}}}{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}O{-}(CH_2)_3{-}Si(OCH_3)_3$$

Similarly

a) $$HS{-}(CH_2)_3{-}Si(OCH_3)_3 \quad + \quad \underset{\text{(propagating radical chain)}}{R^{\bullet}} \rightarrow$$

$$RH + {}^{\bullet}S(CH_2)_3{-}Si(OCH_3)_3$$

b) $${}^{\bullet}S{-}(CH_2)_3{-}Si(OCH_3)_3 + \underset{\text{(acrylate in coating formulation)}}{H_2C{=}CH{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}O{-}R} \rightarrow$$

$$\underset{\text{(new propagating radical)}}{(CH_3O)_3Si{-}(CH_2)_3{-}S^{\bullet}{-}CH_2{-}CH{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}O{-}R}$$

Essentially, it is believed that the adhesion promoter molecule acts as a "link" between the glass surface and the cured inner primary coating: one end having reacted with the glass surface and forming a covalent bond and the other adhesion promoter end reacted into the inner primary coating oligomer network.

The following two U.S. patents disclose examples of radiation-curable, optical glass fiber coating compositions containing adhesion promoters. U.S. Patent No. 4,849,462 describes a coating composition comprising a U.V.-curable polyurethane polyacrylate containing about 0.5 to 5.0 % by weight of a mercapto polyalkoxysilane. U.S. Patent No.

5,146,531 describes an inner primary coating that contains an acrylated urethane oligomer based on a hydrocarbonpolyol, several reactive diluents, an organofunctional adhesion promotor, and a photoinitiator.

Some adhesion promoters are highly susceptible to impurities and contaminants which may be present in the inner primary coating compositions. For example, acidic impurities, or other impurities such as water or alcohol, can react with the adhesion promoters rendering them unreactive with the optical glass fiber surface.

Furthermore, the reaction between the optical glass fiber surface and the adhesion promoter is usually relatively slow. For example, the reaction between the silanic groups on the surface of the optical glass fiber and trialkoxy groups on a silane adhesion promoter may typically require about 24 hours for the reaction to be completed.

There is a need for a solution to the above described instability and unpredictability problems associated with the use of adhesion promoters in radiation-curable, inner primary coating compositions. Moreover, for certain applications, it would be very desirable to easily adjust the strength of adhesion between the inner primary coating and the optical glass fiber, without having to use different inner primary coating compositions. Previous to this invention, if different levels of adhesion between the inner primary coating and sections of the optical glass fiber were desired, then different inner primary coating compositions would have to be used for respective sections of the optical glass fiber, which is difficult to accomplish in practice, time consuming and costly.

In high strength applications, such as the section of optical glass fiber cables for use under deep oceans, the adhesion strength between the inner primary coating and optical glass fiber must be very high. When retrieving the optical glass fiber cable from a deep seabed, very large material forces are applied to the cable and accordingly transmitted to the individual optical glass fibers contained therein. Especially under these conditions, the adhesion between the inner primary coating and optical glass fiber must be relatively quite high and sufficient to preclude some inner primary coatings from sliding detachment from the optical glass fibers under these stresses.

On the other hand, less adhesion between the inner primary coating and the optical glass fiber is desirable at the ends of the cable fibers. It is important to have relatively easy access to the individual optical glass fiber ends with ease of strippability of the inner primary coating from the optical glass fiber.

In such an application, two or more different inner primary, optical glass fiber coating compositions must be used having different levels of adhesion between the inner primary coating and the optical glass fiber.

In ribbon cable applications it is also desirable to provide a low level of adhesion between the inner primary coating and the optical glass fiber so that the inner and outer primary fiber coatings and the matrix material can all be stripped simultaneously from the fiber ends.

When optical glass fibers are to be used in high humidity and hot environments, such as in the southeastern United States, the adhesion between the inner primary coating and the optical glass fiber should again be at a level greater than

normally desired for ribbon cable applications, but less than that desired for deep ocean cable applications.

Thus, there is need for an inexpensive, rapid and facile method for achieving variations in the relative adhesion of the inner primary coating to an optical glass fiber, and which avoids the prior need to use different inner primary coating compositions. Such a method would be very advantageous because only one inner primary coating composition could then be used to permit adjustment of different levels of adhesion over the length of the optical glass fiber.

SUMMARY OF THE INVENTION

An objective of this invention is to provide a solution to the problems associated with the use of adhesion promoters in radiation-curable, inner primary coating compositions.

Another objective of this invention is to provide an inexpensive, rapid and facile method for adjusting the level of adhesion bonding between the inner primary coating and an optical glass fiber, and which avoids the need to use different inner primary coating compositions.

Surprisingly, it has now been found that by exposing the glass fiber as it is drawn from the preform to electron beam radiation, free radicals are apparently formed on the surface of optical glass fiber. Upon application of the inner primary coating to the irradiated glass fiber, bonding of the radiation-curable oligomeric coating composition appears to occur with enhancement of the bonding therebetween. In some cases, the resulting adhesion forces may be of sufficient strength that the use of an adhesion promoter may not be required.

The present invention provides a method of increasing the adhesion of a radiation-cured, inner primary, optical glass fiber coating on an optical glass fiber. The method includes the steps of:

(1) exposing at least a section of the optical glass fiber to electron beam radiation at a level sufficient to induce bonding with a radiation-curable, optical glass fiber coating composition (and with the apparent result of forming at least transient free radicals on the exposed surface of the optical glass fiber);

(2) applying said radiation-curable, optical glass fiber coating composition onto the electron-beam-exposed optical glass fiber, the coating composition containing at least one monomer or oligomer having a radiation-curable functional group which can form free radicals in the presence of actinic radiation; and

(3) exposing the coated optical glass fiber to actinic radiation to thereby cure and bond the inner primary coating.

The present invention also provides a method whereby different respective sections of a coated optical glass fiber exhibit different levels of adhesion between said radiation-cured, inner primary coating and said respective sections of the coated optical glass fiber. That method includes the steps of:

(1) exposing a first section of the optical glass fiber to electron beam radiation having a first amperage level (apparently effective to provide a first quantity of free radicals on the surface of the first exposed section of the optical glass fiber);

(2) exposing a second section of the optical glass fiber to electron beam radiation having a second amperage level different from the first

amperage level (apparently effective to provide a second quantity of free radicals on the surface of the second exposed section of the optical glass fiber);

(3) applying a radiation-curable, optical glass fiber coating composition onto the first and second exposed sections of the optical glass fiber, the coating composition containing at least one monomer or oligomer having a radiation-curable functional group capable of forming free radicals in the presence of actinic radiation; and

(4) exposing the coated optical glass fiber to actinic radiation to cure the coating composition and form an inner primary coating,

wherein the section of the inner primary coating covering the first exposed section exhibits a level of adhesion to the optical glass fiber different from the level of adhesion of the inner primary coating covering the second section.

The present invention further provides a coated optical glass fiber having resistance to delamination caused by moisture. The coated optical glass fiber comprises:

an optical glass fiber having at least a section which has been surface treated by exposure to electron beam radiation at a level sufficient to induce bonding with a radiation-curable, optical glass fiber coating composition (and with the apparent result of forming at least transient free radicals on the exposed surface of the optical glass fiber); and

a radiation-cured inner primary coating on the optical glass fiber which has been coated and suitably cured on the surface

treated optical glass fiber.

The present invention also provides a coated optical glass fiber comprising:

an optical glass fiber having sections which have been surface treated by exposure to different levels of electron beam radiation; and

a radiation-cured inner primary coating on the optical glass fiber which has been coated and suitable cured on the surface treated optical glass fiber,

whereby the sections of the coated optical glass fiber have different levels of adhesion between the radiation-cured inner primary coating and each section of the coated optical glass fiber.

The present invention also provides an optical glass fiber cable which contains a plurality of coated optical glass fibers, at least one of the plurality of coated optical glass fibers being one of above described coated, surface treated optical glass fibers, and a sheath covering the plurality of optical glass fibers.

Another embodiment of the present invention provides a telecommunications system comprising:

at least one of the above described coated, surface treated optical glass fibers;

at least one transmitter connected to the optical glass fiber; and

at least one receiver connected to the optical glass fiber.

A further embodiment of the present invention is an optical glass fiber drawing tower for making a surface treated optical glass fiber coated with an inner primary coating. The drawing

tower can be controlled to continuously adjust the adhesion of the inner primary coating to the surface treated optical glass fiber. The drawing tower comprises:

a furnace for heating a preform and making a bare optical glass fiber:

an electron beam source in a location for contacting the bare optical glass fiber with electron beam radiation;

an inner primary coating applicator for applying an inner primary coating composition to the surface treated optical glass fiber;

a source of actinic radiation for curing the inner primary coating composition; and

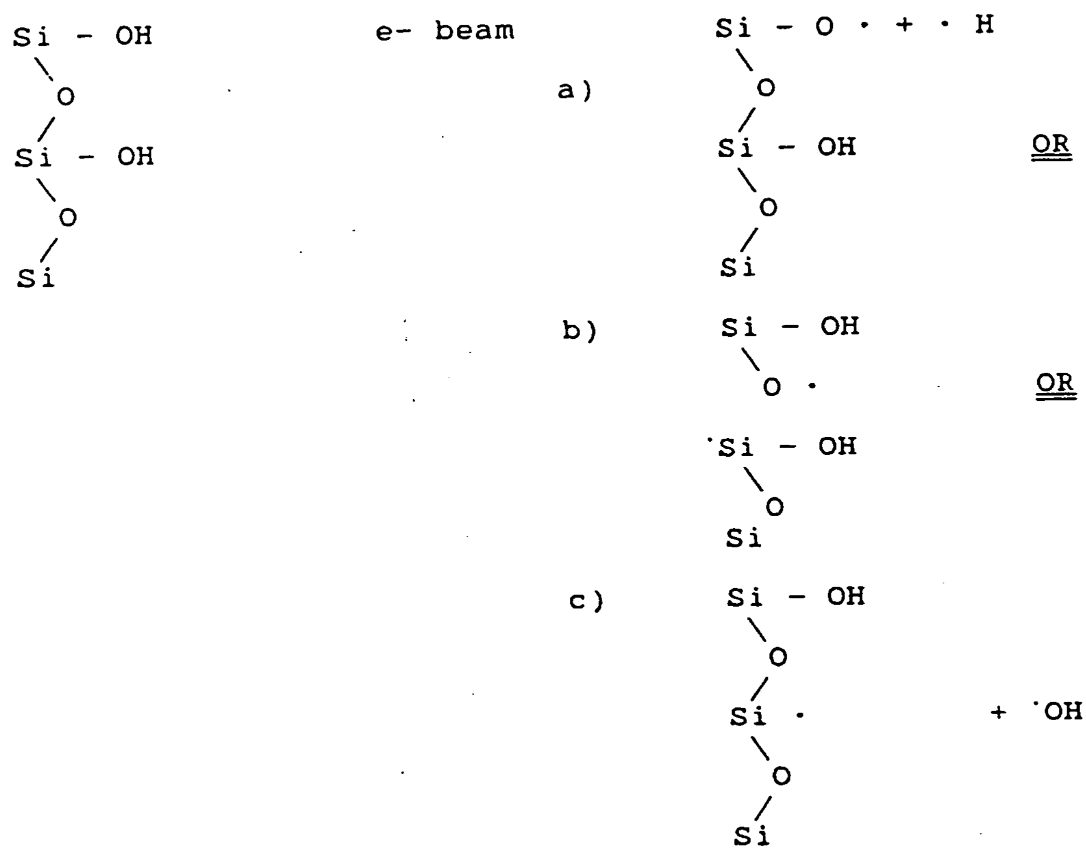
a takeaway for winding the coated optical glass fiber.

BRIEF DESCRIPTION OF THE DRAWING

Fig. 1 is a schematic illustration of an optical glass fiber drawing tower which may be used in practicing the present invention.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

While not wishing to be bound by the following explanation, it is believed that exposure of an optical glass fiber surface to electron beam radiation according to this invention causes the glass matrix chemical bonds to rupture and form free radicals as shown below under a), b) and/or c):



When a radiation-curable, inner primary coating composition is applied to the surface of the surface treated optical glass fiber containing these free radicals and exposed to actinic radiation, the actinic radiation can generate free radicals in the inner primary coating composition which are believed to react with the free radicals present on the surface of the surface treated optical glass fiber. This may preclude the necessity of using an adhesion promoter in inner primary coating compositions, as discussed more fully below.

Alternatively, the free radicals on the surface of the surface treated optical glass fiber may be capable of reacting directly with any ethylenically unsaturated functional groups, such as

acrylate or methacrylate terminal groups, present in the inner primary coating composition.

Inner primary coating composition

This invention is applicable to radiation-curable, inner primary, optical glass fiber coating compositions (hereinafter "inner primary composition") containing a radiation-curable functional group, and optical glass fibers to which these inner primary compositions are applied.

Inner primary compositions usually contain one or more radiation-curable oligomers or monomers having at least one functional group capable of polymerization through radical polymerization when exposed to actinic radiation, such as UV light. Suitable radiation-curable oligomers or monomers are now well known and within the skill of the art.

Commonly, the radiation-curable functionality used is ethylenic unsaturation, which can be polymerized through free radical polymerization. Specific examples of suitable ethylenic unsaturation are groups containing acrylate, methacrylate, styrene, vinylether, vinyl ester, N-substituted acrylamide, N-vinyl amide, maleate esters, and fumarate esters. Preferably, the ethylenic unsaturation is provided by a group containing acrylate, methacrylate, or styrene functionality.

Another type of radiation-curable functionality generally used is provided by, for example, thiol-ene or amine-ene systems. The thiol-ene and amine-ene systems are usually polymerized through free radical polymerization. In the thiol-ene and amine-ene systems, for example, polymerization can occur between a group containing allylic unsaturation and a group containing a tertiary amine or thiol.

The free radicals believed to be generated on the surface of the surface treated optical glass fiber may be able to react directly with the radiation-curable functionality present in the inner primary composition, without first generating free radicals in the inner primary composition. However, the coating composition is preferably exposed to actinic radiation to generate free radicals therein. The free radicals generated in the coating composition are believed to react with the free radicals generated on the surface of the surface treated optical glass fiber.

The inner primary compositions may also contain a reactive diluent which can be used to adjust the viscosity of the inner primary composition. The reactive diluent can be a low viscosity monomer having at least one functional group capable of polymerization when exposed to actinic radiation. This functional group may be of the same nature as that used in the radiation-curable monomer or oligomer. Preferably, the functional group present in the reactive diluent is capable of copolymerizing with the radiation-curable functional group present on the radiation-curable monomer or oligomer. More preferably, the radiation-curable functional group forms free radicals during curing which can react with the free radicals generated on the surface of the surface treated optical glass fiber.

For example, the reactive diluent can be a monomer or mixture of monomers having an acrylate or vinyl ether functionality and an C_4-C_{20} alkyl or polyether moiety. Particular examples of preferred reactive diluents include: hexylacrylate, 2-ethylhexylacrylate, isobornylacrylate, decyl-acrylate, laurylacrylate, stearylacrylate, 2-ethoxyethoxy-ethylacrylate,

laurylvinylether, 2-ethylhexylvinyl ether, N-vinyl formamide, isodecyl acrylate, isooctyl acrylate, vinyl-caprolactam, N-vinylpyrrolidone, and the like.

Another type of reactive diluent that can be used is a compound having an aromatic group. Particular examples of reactive diluents having an aromatic group include:
ethyleneglycolphenylether-acrylate, polyethyleneglycolphenyletheracrylate, polypropyleneglycolphenylether-acrylate, and alkyl-substituted phenyl derivatives of the above monomers, such as polyethyleneglycolnonylphenyl-etheracrylate, and polypropyleneglycolnonyl-phenyletheracrylate.

The reactive diluent can also comprises a diluent having two or more functional groups capable of polymerization. Particular examples of such monomers include:
C_2–C_{18} hydrocarbon-dioldiacrylates,
C_4–C_{18} hydrocarbondivinylethers,
C_3–C_{18} hydrocarbon triacrylates, and the polyether analogues thereof, and the like, such as 1,6-hexanedioldiacrylate, trimethylolpropanetri-acrylate, ethoxylated trimethylolpropane tri-acrylate, hexanedioldivinylether, triethylene-glycoldiacrylate, pentaerythritol-triacrylate, ethoxylated bisphenol-A diacrylate, and tripropyleneglycol diacrylate.

If the radiation-curable functional group of the radiation-curable monomer or oligomer has an amine-ene or thiol-ene system, examples of reactive diluents having allylic unsaturation that can be used include:
diallylphthalate, triallyltri-mellitate, triallylcyanurate, triallylisocyanurate, and diallylisophthalate. For amine-ene systems, amine functional diluents that can be used include, for

example:
the adduct of trimethylolpropane, isophorondiisocyanate and di(m)ethylethanolamine,
the adduct of hexanediol, isophorondiisocyanate and dipropylethanolamine, and
the adduct of trimethylol propane, trimethylhexamethylene diisocyanate and di(m)ethylethanolamine.

The inner primary compositions also usually contain an adhesion promoter which has glass-binding groups that are capable of bonding to optical glass fiber under the curing conditions for the particular application of the inner primary composition to the optical glass fiber. Such inner primary coating compositions containing adhesion promoters can be used in this invention, but the use of an adhesion promoter may be unnecessary. This invention can provide a bond or "link" between the cured inner primary coating and the surface treated optical glass fiber. Therefore, there may not be a need for further "links" between the cured inner primary coating and the surface treated optical glass fiber, such as those previously only provided by adhesion promoters. Thus, preferably, the inner primary coating composition used is substantially-free of an adhesion promoter, which avoids many of the problems associated with the use of adhesion promoters.

Other additives which can be used in the inner primary composition include, but are not limited to, light sensitive and light absorbing components, photoinitiators, catalysts, lubricants, wetting agents, antioxidants and stabilizers. The selection and use of such additives is within the skill of the art.

Photoinitiators can be used in the inner primary coating composition. However, because the

free radicals believed to be generated on the surface of the optical fiber may react with the radiation-curable functionality present in the inner primary composition, the use of photoinitiators can be minimized or eliminated. Photoinitiators can be reduced to less than 2%wt or more preferably to less than 1 %wt and may not be required at all.

Use of the electron beam

This invention provides a very flexible method for easily and quickly adjusting the level of adhesion between the inner primary coating and the surface treated glass optical fiber. This adhesion can even be adjusted continuously as the coated, surface treated optical glass fiber is being produced on a drawing tower to provide many different levels of adhesion between the inner primary coating and the surface treated optical glass fiber.

The level of adhesion between the inner primary coating and the surface treated optical glass fiber is believed to be mainly dependent upon the following factors:

(1) the amperage level of electron beam radiation striking the surface of the optical glass fiber; and
(2) the structure of the monomers and oligomers present in the inner primary coating composition.

In general, the greater the amperage level of electron beam radiation striking the surface of the optical glass fiber the greater the adhesion that is induced between the inner primary coating and the surface treated optical glass fiber. It is believed that the greater the amperage level of electron beam radiation striking the surface of the optical glass fiber the greater the quantity of free

radicals generated on the surface of the surface treated optical glass fiber. It is also believed that the quantity of free radicals on the surface of the surface treated optical glass fiber during curing of the inner primary coating is dependent upon the quantity of free radicals generated on the surface of the optical glass fiber during exposure to the electron beam radiation less the amount of free radicals which are scavenged by free radical scavengers or oxygen before curing the inner primary coating and less the amount of free radicals that reform the bonds that were broken on the surface of the surface treated optical glass fiber.

The amperage level of the electron beam radiation striking the optical glass fiber can be easily adjusted, including, but not limited to, the following:

(1) varying the amount of time the surface of the optical glass fiber is exposed to the electron beam radiation; and

(2) varying the power density of the electron beam radiation striking the surface of the optical glass fiber.

The amount of time the surface of the optical glass fiber is exposed to the electron beam radiation can easily be adjusted by varying the speed the optical glass fiber passing through the electron beam. In general, the faster the speed of the optical glass fiber, the lower the amperage level of the electron beam radiation striking the surface of the optical glass fiber and the less adhesion that is induced between the surface treated optical glass fiber and the inner primary coating (and apparently the less free radicals generated on the surface of the surface treated optical glass fiber).

The amperage level of the electron

beam can be easily adjusted, for example, by adjusting the focus of the beam, electronically adjusting the amperage output of the electron beam, or by using filters.

Preferably, the amperage level of the electron beam radiation striking the optical glass fiber should be selected to provide the minimum amount of surface treatment required to induce the desired level of adhesion between the inner primary coating and the surface treated optical glass fiber, to reduce the possibility of damaging the optical glass fiber. If the amperage level of the electron beam striking the optical glass fiber is too high, permanently colored regions within the core of the surface treated optical glass fiber may be formed which can cause attenuation of the signal transmission through the surface treated optical glass fiber, or other undesirable effects.

Optical glass fibers have many different additives which can be affected by electron beam radiation. Thus, the amperage level of the electron beam radiation that is suitable will usually be dependent upon the specific optical glass selected. One skilled in the art will easily be enabled to test the selected optical glass fiber by exposure to different electron beam radiation power levels to determine which amperage levels are suitable for the selected optical glass fiber, without undue experimentation.

The level of adhesion between the inner primary coating and the surface treated optical glass fiber may also be dependent upon the formulation of the inner primary composition. Inner primary coatings usually have a low equilibrium modulus. In general, a low equilibrium modulus is usually achieved by selecting monomers having fewer radiation-curable functional groups per volume unit.

A low equilibrium modulus can also be achieved by reducing the concentration of the radiation-curable functional groups present in the inner-primary composition. Inner primary compositions having a lower concentration radiation-curable functional groups are believed to have fewer groups that can form "links" with the surface treated optical glass fiber, and/or apparently, with any free radicals present on the surface of the surface treated optical glass fiber. It is believed that the fewer the "links" between the inner primary coating and the surface treated optical glass fiber, the lower the level of adhesion between the inner primary coating and the surface treated optical glass fiber.

Furthermore, the different types of radiation-curable functional groups react differently in the presence of actinic radiation during curing. In general, those radiation-curable functional groups which are more reactive with free radicals in the presence of actinic radiation will result in greater adhesion between the inner primary coating and the surface treated optical glass fiber.

Based on the disclosure herein, one skilled in the art will easily be enabled to test the adhesion between the selected inner primary coating and the selected optical glass fiber to determine the optimum amperage level of the electron beam radiation needed to provide the desired adhesion, without undue experimentation.

To maximize the effect of the surface treatment (and apparently the quantity of free radicals present on the surface of the surface treated optical glass fiber during curing of the inner primary coating), the steps of exposing the surface of the optical glass fiber to electron beam radiation and applying the inner primary composition onto the surface treated optical glass fiber are

preferably conducted in an atmosphere which is substantially free of free radical scavengers and oxygen. Examples of suitable atmospheres include inert gasses, such as nitrogen, neon, or argon gas.

The surface treatment of the surface treated optical glass fiber may become less effective with the passage of time. This may be due to the quantity of free radicals on the surface of the surface treated optical glass fiber being diminish by the reformation of bonds which were broken on the surface of the surface treated optical glass fiber. Thus, preferably the inner primary coating is applied and cured on the surface treated optical glass fiber as soon as possible after the surface of the optical glass fiber is exposed to electron beam radiation.

Because the adhesion between the inner primary coating the surface treated optical glass fiber is dependent upon the amperage level of the electron beam radiation, the adhesion can be continuously varied. For example, during drawing of the optical glass fiber, the moving uncoated optical glass fiber can be exposed to varying amperage levels of electron beam radiation to provide different levels of surface treatment on the optical glass fiber. In general, those sections of the surface treated optical glass fiber that have been exposed to greater amperage levels of electron beam radiation will result in more adhesion between the inner primary coating and the surface treated optical glass fiber, than those sections of the surface treated optical glass fiber that have been exposed to lower amperage levels of electron beam radiation. In this manner, the different levels of adhesion can be easily provided without stopping the fiber drawing process and changing the inner primary coating composition. For example, an undersea

optical glass fiber can be easily provided with greater adhesion between the optical glass fiber and inner primary coating for those sections to be used under the deep sea, and the end sections can be provided with less adhesion between the optical glass fiber and the inner primary coating to facilitate ease of forming connections.

Another example of providing sections of the coated optical glass fiber with different levels of adhesion between the optical glass fiber and the inner primary coating, is to leave the end sections of the optical glass fiber untreated and provide a sufficient amount of adhesion promoter in the radiation-curable, inner primary composition to provide a radiation-cured inner primary coating having strippability and sufficient adhesion to prevent delamination. The central section of the optical glass fiber can then be surface treated according to the present invention to provide enhanced levels of adhesion between the inner primary coating and the optical glass fiber.

The coated, surface treated optical glass fibers made according to this invention can be used in telecommunication systems. Such telecommunication systems typically include cables containing optical glass fibers, transmitters, receivers, and switches. The cables containing the optical glass fiber are the fundamental connecting units of telecommunication systems.

The coated, surface treated optical glass fibers made according to this invention can be adapted for enclosure within a cabled structure. The cabled structure can be buried under ground or water for long distance connections, such as between cities. Alternatively, the coated, surface treated optical glass fibers can be adapted for use in local area networks, such as for connecting offices in

high rise buildings, residential subdivisions, and the like. Furthermore, the coated, surface treated optical glass fibers can be adapted for use in ribbon cable applications. One skilled in the art will easily be enabled to adapt the coated, surface treated optical glass fibers for the desired application. For example, such a person knows what level of adhesion is required between the inner primary coating and the optical glass fiber for the desired application. Based on the disclosure herein, such a person will easily be enabled to provide that required level of adhesion.

This invention also relates to a novel drawing tower which provides flexibility in providing different levels of adhesion between the inner primary coating and a surface treated optical glass fiber, while avoiding the undesirable necessity of stopping the fiber drawing process and changing the inner primary coating composition.

Fig. 1 shows a schematic illustration of a drawing tower apparatus which can be used to practice the claimed invention. In Fig. 1, the preform shown at 1 is heated in the furnace shown at 2 to produce an uncoated optical glass fiber 3. The uncoated optical glass fiber 3 then passes through an electron beam generating apparatus shown at 4 to surface treat the bare optical glass fiber 3. The electron beam generating apparatus 4 preferably includes a controller (not shown) for controlling the amperage level of the electron beam. Then, an inner primary composition is applied to the surface treated bare optical glass fiber using the coating applicator shown at 5. The inner primary coating is cured by exposure to actinic radiation, which is shown at 6. An outer primary composition is then applied to the cured inner primary coating using the coating applicator shown at 7. The outer primary

composition is cured by exposure to actinic radiation, shown at 8. The thus coated optical glass fiber is then wound by a takeaway, as shown at 9. The amperage level of the electron beam shown at 4 is preferably controllable to provide the desired amperage level of electron beam exposure to the optical glass fiber. Electron beam sources have been used by those skilled in the art to cure the coating compositions applied to optical glass fibers. Thus, one skilled in the art is familiar with the use of such electron beam sources. These same electron beam sources can be used to practice the claimed invention. For example, high energy, low voltage electron beam sources, such as Min-EB™, commercially available from American International Technologies, Torrence, California, can be used. Instead of applying the electron beam to cure a radiation-curable coating, the electron beam is now being used to surface treat the bare optical glass fiber. Thus, based on the disclosure herein, one skilled in the art will easy be enabled to modify known glass optical fiber drawing towers and move the electron beam source from downstream of the radiation-curable, coating composition applicators, to a location where the electron beam radiation can strike the bare optical glass fiber, as shown in Fig. 1. Such a person will also be easily enabled to select suitable power levels for the electron beam, based on the disclosure provided herein.

U.S. patent nos. 4,324,575, 4,962,992, and Re. 33,677 disclose suitable optical glass fiber drawing towers that can be modified according to this invention. The disclosure of these three patents is incorporated herein by reference.

C L AI M S

1. A method of increasing the adhesion of a radiation-cured, inner primary, optical glass fiber coating on an optical glass fiber, said method comprising the steps of:
(1) exposing at least a section of said optical glass fiber to electron beam radiation at a level sufficient to induce bonding with a radiation-curable, optical glass fiber coating composition;
(2) applying said radiation-curable, optical glass fiber coating composition onto said electron beam exposed optical glass fiber, said coating composition containing at least one monomer or oligomer having a radiation-curable functional group which can form free radicals in the presence of actinic radiation; and
(3) exposing said coated optical glass fiber to actinic radiation to thereby cure said inner primary coating.

2. A method according to claim 1, wherein step (1) is conducted in a manner to provide free radicals on said optical glass fiber surface and step (3) is conducted in a manner to provide free radicals in said coating composition wherein said free radicals in said coating composition react with said free radicals present on said optical glass fiber.

3. A method according to any one of claims 1-2, wherein said radiation-curable, inner primary coating composition contains a monomer or oligomer having an acrylate or methacrylate functionality.

4. A method according to any one of claims 1-3, further comprising the step of drawing said

optical glass fiber from a preform, and then conducting said steps (1) through (3) in a continuous process.

5. A method according to any one of claims 1-4, wherein a power level of said electron beam radiation in step (1) is high enough to induce bonding between said optical glass fiber and said inner primary coating composition, and is low enough to prevent the formation of colored regions that can cause attenuation of the signal transmission in said optical glass fiber.

6. A method according to any one of claims 1-5, wherein said steps (1) through (3) are conducted in an atmosphere substantially free of free radical scavengers or oxygen.

7. A method according to any one of claims 1-6, wherein said radiation-curable, inner primary coating composition is substantially free of a silane glass coupling agent.

8. A method of providing different sections of a coated optical glass fiber with different levels of adhesion between a radiation-cured, inner primary coating and each section of said coated optical glass fiber, said method comprising the steps of:

(1) exposing a first section of said optical glass fiber to electron beam radiation having a first amperage level sufficient to induce bonding with a radiation-curable, optical glass fiber coating composition;

(2) applying said radiation-curable, optical glass fiber coating composition onto said first section of said optical glass fiber, said coating composition containing at least one monomer or oligomer having a

radiation curable functional group which can form free radicals in the presence of actinic radiation; and

(3) exposing said first section of said optical glass fiber to actinic radiation to cure said coating composition and form an inner primary coating;

(4) exposing a second section of said optical glass fiber to electron beam radiation having a second amperage level sufficient to induce bonding with said radiation-curable, optical glass fiber coating composition, said second amperage level being different from said first amperage level;

(5) applying said radiation-curable, optical glass fiber coating composition onto said second section of said optical glass fiber, said coating composition containing at least one monomer or oligomer having a radiation curable functional group which can form free radicals in the presence of actinic radiation; and

(6) exposing said second section of said optical glass fiber to actinic radiation to cure said coating composition and form an inner primary coating,

wherein the section of said inner primary coating covering said first section has a different level of adhesion to said optical glass fiber than the section of said inner primary coating covering said second section.

9. A coated optical glass fiber having resistance to delamination caused by moisture, said coated optical glass fiber comprising:

an optical glass fiber having at least one

section which has been surface treated by exposure to an electron beam radiation at a level sufficient to induce bonding with a radiation-curable, optical glass fiber coating composition; and

a radiation-cured inner primary coating on said optical glass fiber, said radiation-cured inner primary coating being formed from said radiation-curable, optical glass fiber coating composition.

10. A coated optical glass fiber comprising:

an optical glass fiber having sections which have been surface treated by exposure to different amperage levels of electron beam radiation; and

a radiation-cured inner primary coating on said optical glass fiber which has been suitably cured,

whereby said different sections of said coated optical glass fiber have different levels of adhesion between said radiation-cured inner primary coating and each section of said coated optical glass fiber.

11. An optical glass fiber cable comprising;

(1) a plurality of coated optical glass fibers containing at least one coated optical glass fiber comprising:

(i) an optical glass fiber having at least one section which has been surface treated by exposure to electron beam radiation at a level sufficient to induce bonding with a radiation-curable, optical glass fiber coating composition; and

(ii) a radiation-cured inner primary coating on said optical glass fiber, said radiation-cured inner primary coating being formed from said radiation-curable,

optical glass fiber coating composition which has been suitably cured; and

(2) a sheath covering said plurality of optical glass fibers.

12. An optical glass fiber cable comprising;

(1) a plurality of coated optical glass fibers containing at least one coated optical glass fiber comprising:

(i) an optical glass fiber having sections which have been surface treated by exposure to different amperage levels of electron beam radiation; and

(ii) a radiation-cured inner primary coating on said optical glass fiber which has been suitably cured,

wherein said different sections of said coated optical glass fiber have different levels of adhesion between said radiation-cured inner primary coating and each section of said coated optical glass fiber; and

(2) a sheath covering said plurality of optical glass fibers.

13. A telecommunications system comprising:

at least one coated optical glass fiber having resistance to delamination caused by moisture, said coated optical glass fiber comprising:

an optical glass fiber having at least one section which has been surface treated by exposure to electron beam radiation at a level sufficient to induce bonding with a radiation-curable, optical glass fiber coating composition; and

a radiation-cured inner primary coating on said optical glass fiber which has been formed from said radiation-curable optical glass fiber coating composition;

at least one transmitter connected to said at least one optical glass fiber; and

at least one receiver connected to said at least one optical glass fiber.

14. A telecommunications system comprising:

at least one coated optical glass fiber comprising:

an optical glass fiber having sections which have been surface treated by exposure to different amperage levels of electron beam radiation; and

a radiation-cured inner primary coating on said optical glass fiber which has been suitably cured,

wherein said different sections of said coated optical glass fiber have different levels of adhesion between said radiation-cured inner primary coating and each section of said coated optical glass fiber;

at least one transmitter connected to said at least one optical glass fiber; and

at least one receiver connected to said at least one optical glass fiber.

15. An optical glass fiber drawing tower for making a surface treated, optical glass fiber coated with an inner primary coating, said drawing tower being controllable to continuously adjust the adhesion of said inner primary coating to said surface treated optical glass fiber, said drawing tower comprising:

means for heating a preform and providing an uncoated optical glass fiber;

means for generating an electron beam for irradiating said uncoated optical glass fiber at a radiation level sufficient to induce subsequent bonding between said

optical glass fiber and a radiation-curable, optical glass fiber coating composition;

means for applying an uncured, radiation-curable, inner primary coating composition to said surface treated optical glass fiber;

means for applying actinic radiation to said inner primary coating composition on said optical glass fiber to effect a curing thereof; and

take-up means for winding said coated optical glass fiber.

16. A drawing tower according to claim 15, further comprising controller means for controlling the amperage level of said electron beam.

17. In an optical glass fiber drawing including:

means for heating a preform and providing an uncoated optical glass fiber;

means for applying an uncured, radiation-curable, inner primary coating composition to said surface treated optical glass fiber;

means for applying actinic radiation to said inner primary coating composition on said optical glass fiber to effect a curing thereof; and

take-up means for winding said coated optical glass fiber;

the improvement consisting essentially of including further means for generating an electron beam for irradiating said uncoated optical glass fiber at a radiation level sufficient to induce subsequent bonding between said optical glass fiber and a radiation-curable, optical glass fiber coating composition;

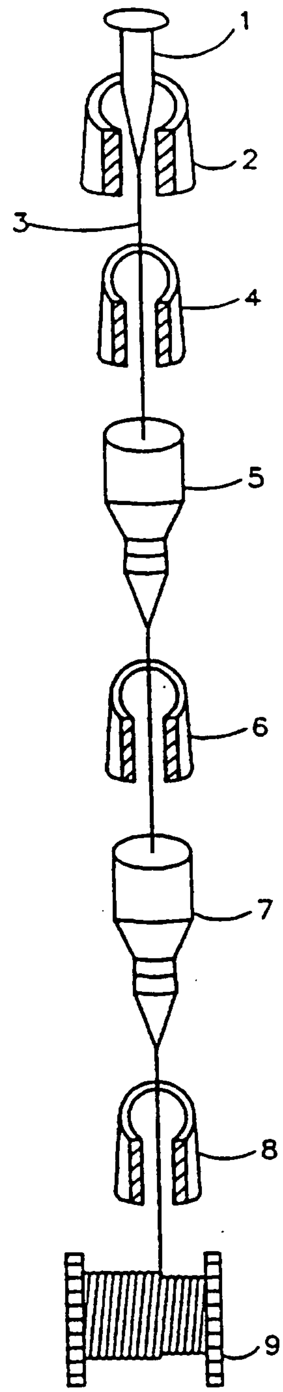
and wherein said improved optical glass fiber drawing tower being controllable to continuously adjust the adhesion of said inner primary coating to said surface treated optical glass fiber

18. A coated glass article having resistance to delamination caused by moisture, said coated glass article comprising:

a glass article having at least one section which has been surface treated by exposure to an electron beam radiation at a level sufficient to induce bonding with a radiation-curable, glass coating composition; and

a radiation-cured coating on said glass article, said radiation-cured inner coating being formed from said radiation-curable, glass coating composition.

FIG. 1



INTERNATIONAL SEARCH REPORT

Inte[...]onal Application No
PCT/NL 97/00175

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C03C25/02 C03C25/00 B01J19/08

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C03C B01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	GB 2 155 357 A (STANDARD TELEPHONES CABLES LTD) 25 September 1985 see the whole document ---	1-18
A	DATABASE WPI Section Ch, Week 8527 Derwent Publications Ltd., London, GB; Class L01, AN 85-161558 XP002033865 & JP 60 090 853 A (FURUKAWA ELECTRIC CO LTD) , 22 May 1985 see abstract --- -/--	1-18

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

* Special categories of cited documents :

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"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

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Date of the actual completion of the international search	Date of mailing of the international search report
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Name and mailing address of the ISA	Authorized officer
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DATABASE WPI Section Ch, Week 8548 Derwent Publications Ltd., London, GB; Class A89, AN 85-298718 XP002033866 & JP 60 204 641 A (NIPPON TELEGRAPH & TELEPHONE CORP) , 16 October 1985 see abstract ---	1-18
A	JOURNAL OF NON-CRYSTALLINE SOLIDS, vol. 188, no. 1/02, 2 July 1995, pages 87-92, XP000511341 DUDKO Y V ET AL: "ELECTRON-BEAM MODIFICATION OF SILICATE GLASS SURFACES" see paragraph 1 see paragraph 5 -----	1-18

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/NL 97/00175

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
GB 2155357 A	25-09-85	NONE	